

Corrosion rates and negative difference effects for Al and some Al alloys*

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The rotating disc-ring technique with a Pt ring was used to quantitatively detect hydrogen evolved on an Al-disc electrode during spontaneous corrosion at open-circuit potential or during anodic polarization of an Al disc to study the unusual increase of H_2 evolution with increase in anodic current (the so called negative difference effect). Experiments were made with high purity Al (99.999%), technical grade Al (99.5%) (Al-T) and Al-In alloy (0.074% In) in deaerated 0.5 M aqueous NaCl solution (pH \sim 6.5) and NaCl solutions acidified with HCl to pH values of 3.0, 2.0 and 1.0. It was shown, in neutral solutions, that the corrosion rates of all three materials are controlled by the rate of water molecule dissociation or in more acid solutions, by the combined water molecule dissociation rate and H^+ ion discharge rate. The corrosion rates of all three materials in the range of 3–10 $\mu A cm^2$, was the lowest for 99.999% Al. The impurities in Al-T and Al-In increase the hydrogen evolution rate at cathodic polarizations in a similar manner, but very differently affect the negative difference effect. High purity Al and Al-T have a similar negative difference effect (8–15%), while the presence of In decreases it to only about 1%. No pitting and no negative difference effect were observed at potentials more negative than E_{pit} . Therefore, the negative difference effect is connected with the anodic pitting dissolution mechanism. Several aspects of this problem are discussed in more detail.

Keywords: corrosion, corrosion rates, aluminium, aluminium alloys, pitting, faradaic efficiency

1. Introduction

An elaborate study of the electrochemical behaviour of Al in neutral aqueous NaCl solutions showed that over a wide range of potentials between -2 to -0.6 V vs SCE which covers both the cathodic and anodic potential range for aluminium, H_2 evolution proceeds by three different mechanisms [1], by H_2O direct discharge, H_2O dissociation and by coevolution of hydrogen during the anodic Al dissolution (the negative difference effect [2]). Also, it has been shown that the rate of Al corrosion is controlled by the rate of H_2O molecules dissociation (i.e., it is a potential independent process), while Al dissolves through a compact oxide film [1, 3]. Acidifying the NaCl solutions increases both the Al dissolution and H^+ ion discharge processes, which increase the overall corrosion rates [4]. Measuring the corrosion rates of Al presents serious experimental problem, since at corrosion rates of few microamperes per cm^2 the volumetric determination of H_2 gas is impossible, while the weight loss method involves removal of the newly formed oxide layer, which is a very questionable procedure.

Hydrogen coevolution at anodic potentials (i.e., the negative difference effect) is usually measured by

collecting the evolved H_2 gas [5], but this can only be done when the anodic current densities are larger than 5–10 $mA cm^{-2}$. At lower current densities this cannot be done because of the very small amount of evolved hydrogen and its dissolution into the electrolyte.

Our previous investigations [6] have shown that small quantities of hydrogen, evolved during an electrochemical process, can be reliably detected using the disc-ring technique with a Pt ring. Therefore, in this paper we applied the Al-disc/Pt-ring technique to study the corrosion rates and negative difference effects for three Al materials in 0.5 M NaCl at four pH values covering the neutral and acidic range. Results of the similar investigation with high purity Al are presented elsewhere [7] and are incorporated also in this paper for the sake of comparison and to point out the effects of alloying components or impurities.

2. Experimental details

Experiments were performed with high purity Al (Alcan, 99.999%), Al-In alloy (high purity Al + 0.074% In) and technical grade Al (Al-T) (99.5% Al, 0.33% Fe, 0.07% Si, 0.031% Zn, 0.005% Cu). An Al-disc/Pt-ring arrangement (Al-disc 0.2 cm^2 , Pt-ring 0.18 cm^2) with a PINE rotation system was

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used, at rotation speed 1600 rpm. The collection efficiency for the geometry of the used disc–ring system was calculated [8, 9] to be $N = 0.283$, while the experimentally determined value using the $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ system [10] was $N_{\text{exp}} = 0.28 \pm 0.02$. The disc was interchangeable and the above mentioned materials served as the disc. Before each experiment the disc and ring surfaces were polished with SiC paper (1000 grit) and washed with distilled water in an ultrasonic bath.

As explained elsewhere the ring potential was kept at -0.1 V vs SCE to secure the efficient anodic oxidation of hydrogen transported from the Al disc. This potential corresponds to the limiting current of oxidation of hydrogen transported from the disc where hydrogen evolves or is being coevolved during the anodic polarization of Al [6] and since the limiting plateau was larger than 0.5 V changes of solution pH in the experiments performed did not affect the value of the limiting current. The counter electrode was a platinum foil while a saturated calomel electrode (SCE) served as the reference electrode. All the potentials are expressed on the SCE scale.

All the experiments were performed in 0.5 M NaCl solution (Merck and doubly distilled water), at room temperature ($22 \pm 2^\circ \text{C}$). The solution pH was adjusted in the range 6.5 to 1.0 by addition of HCl. The solutions were deaerated all the time with purified nitrogen.

Prior to the experiments the electrodes were in contact with the solution for 60 min. Immediately before the ring measurement Pt was anodically polarized to 0.6 V for 1 min in order to clean the surface, as prescribed for the proper use of the method of hydrogen detection by the ring technique [6].

3. Results

Figure 1 shows the anodic polarization curve for the high purity Al-disc in a deaerated sodium chloride solution as well as the anodic H_2 oxidation current densities simultaneously registered on the Pt ring during the disc dissolution. It can be seen that the Pt-ring detects the hydrogen evolution rate (i.e., corrosion rate) at the open circuit (corrosion) potential ($E_{\text{cor}} \approx -1.15 \text{ V}$, $i_{\text{cor}} = 3.0 \mu\text{A cm}^{-2}$) with a very small decrease in the hydrogen evolution rate between the corrosion potential and the pitting potential ($E_{\text{pit}} \approx -0.75 \text{ V}$), and a large increase in the ring current, that is, hydrogen evolution after the pitting potential. At the same time, the anodic Al disc current also has two characteristic potential regions with a rather small rate of increase between E_{cor} and E_{pit} , and a sudden rise after the pitting potential. Obviously, this sudden increase in the anodic current is coupled with the increase in the Pt ring current (i.e., hydrogen evolution). As mentioned previously, this is a phenomenon named the negative difference effect, that is, the system behaves opposite to the expectations based on the classic Wagner–Traud approach [11].

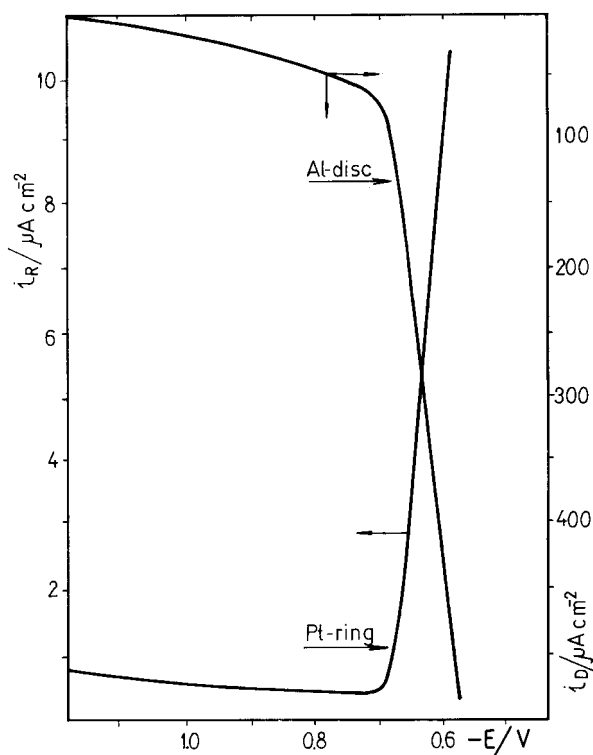


Fig. 1. Potentiodynamic anodic polarization curve for Al in deaerated NaCl solution, at scanning rate $v = 10 \text{ mV s}^{-1}$ (Al disc). Simultaneous hydrogen evolution current detected at Pt ring by H_2 oxidation at $E_{\text{ring}} = 0.1 \text{ V}$ vs SCE.

The results presented in Fig. 1 were obtained in one of ten experiments repeated under the same conditions. However, the measured ring currents in these ten experiments varied between 2.5 and $8.5 \mu\text{A cm}^{-2}$, showing that the measured corrosion rates varied for reasons as yet not identified. Therefore, the experiments at each pH were repeated ten times and the mean values are shown in Fig. 2 for pH

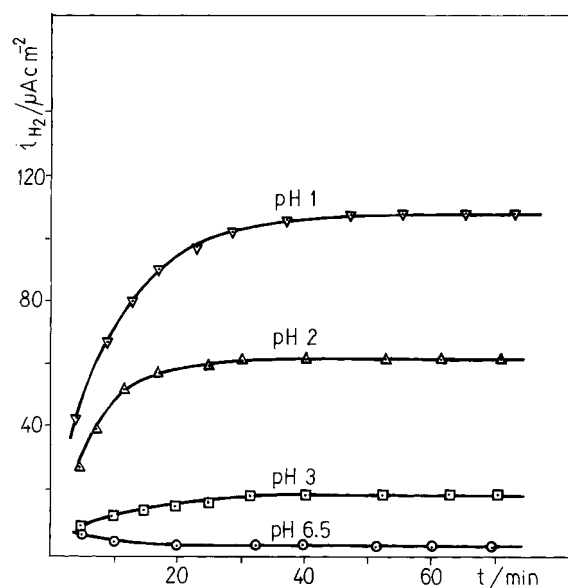


Fig. 2. Change of the hydrogen evolution current density (i.e., corrosion rate), of Al disc over time, at the corrosion potential detected on the Pt ring, for different pH's. Ring potential, $E_{\text{ring}} = -0.1 \text{ V}$ vs SCE.

6.5, 3.0, 2.0 and 1.0. Figure 2 also shows that the steady state corrosion rates are established only after more than 60 min, that is, except for pH 6.5, there is a considerable increase in the corrosion rates from the moment of contact of the Al with the electrolyte and after about 60 min. Obviously this is in some way connected with the changes in the properties of the Al-electrolyte interphase, most probably with the properties of the oxide film.

The Pt-ring current can also be followed during the cathodic polarization of the Al disc. A simultaneous recordings of these two currents in 0.5 M NaCl solution are shown in Fig. 3. If the disc-ring system is functioning properly, the evolved hydrogen on the Al disc should be collected with a proper efficiency on the Pt ring. The proof of this is shown in Fig. 4 which shows the simultaneous recordings of the Al disc and Pt ring current densities in 0.5 M NaCl solutions, when the potential was scanned from -1.7 to -0.7 V. As can be seen, during the cathodic polarization, that is, when the disc was more negative than E_{cor} , the directly measured disc current densities (open circles) and from the measured ring currents properly recalculated ($i_{\text{H}_2} = i_{\text{ring}}/N$ using $N = 0.28$) ring H_2 detection current densities (black circles) almost coincide. Differences between these two current densities appear only during anodic polarization of the Al disc. In fact, these data are the same as those shown in Fig 1, but with semilogarithmic coordinates. The anodic Al disc current showed a Tafel type behaviour with a rather high value of the Tafel slope

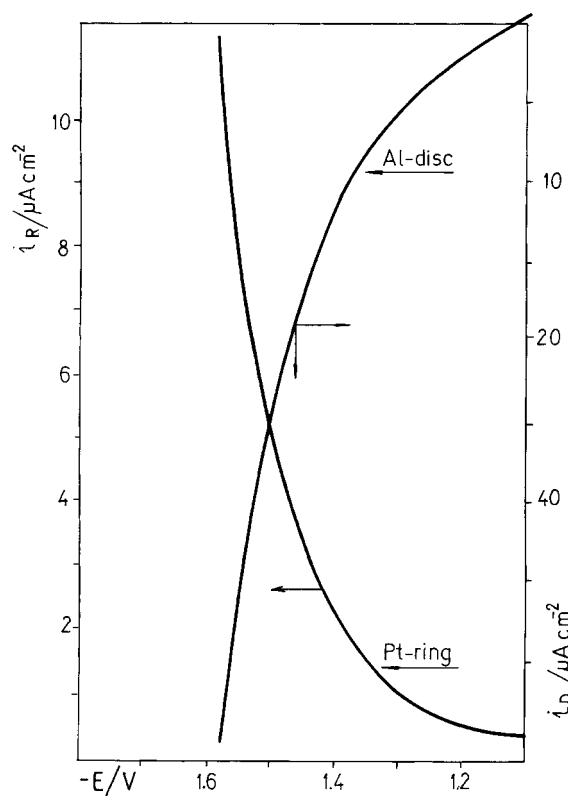


Fig. 3. Potentiodynamic cathodic polarization curve for Al in NaCl solution at scanning rate 10 mV s^{-1} (Al disc). Simultaneous hydrogen evolution current detected at Pt ring (Pt ring).

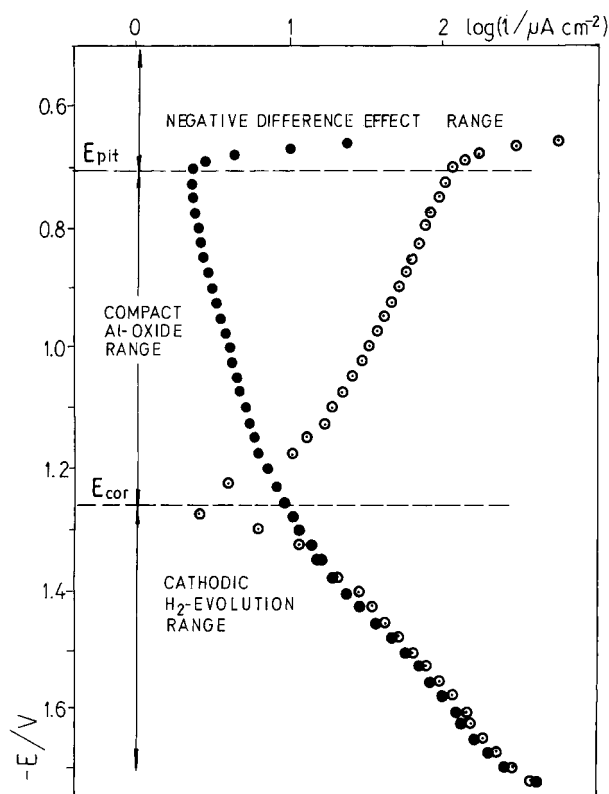


Fig. 4. Cathodic and anodic polarization curves for high purity Al in deaerated NaCl solution (open circles) and simultaneous hydrogen evolution rates detected on the Pt ring (black dots).

($\sim 400 \text{ mV dec}^{-1}$), as also shown elsewhere [1], and an almost horizontal part at potentials more positive than E_{pit} . During anodic polarization the hydrogen evolution current density decreases slightly, although not as much as expected by the theory [11] and suddenly increases following the increase in the Al dissolution current.

The effects of changing the pH of the 0.5 M NaCl solution, by addition of adequate amounts of HCl are interesting. They are shown in Fig. 5 for the pH values 1.0, 2.0 and 3.0. On the anodic side there is practically no dependence of the Al dissolution rate on pH in this pH range. However, the hydrogen evolution current depends on the pH both on the cathodic and anodic side. On the cathodic side increasing the H^+ ion concentration results in an increase in the cathodic current density, that is, the reaction order for H^+ ions is about one as is to be expected for a charge transfer controlled reaction. On the anodic side, there is a small decrease in the hydrogen evolution rate with increasing Al dissolution rate, similar to that observed in a neutral 0.5 M NaCl solution, (Fig. 4), but again not in accord with the Wagner-Traud mixed potential theory (for pH 1.0, the expected hydrogen evolution rate in the anodic Al dissolution domain is shown by a dashed line). Previously [3], we proposed that this type of phenomenon can be explained by the water dissociation rate determining hydrogen evolution mechanism which is expected to be a potential independent process and which, in neutral solutions, controls the Al corrosion

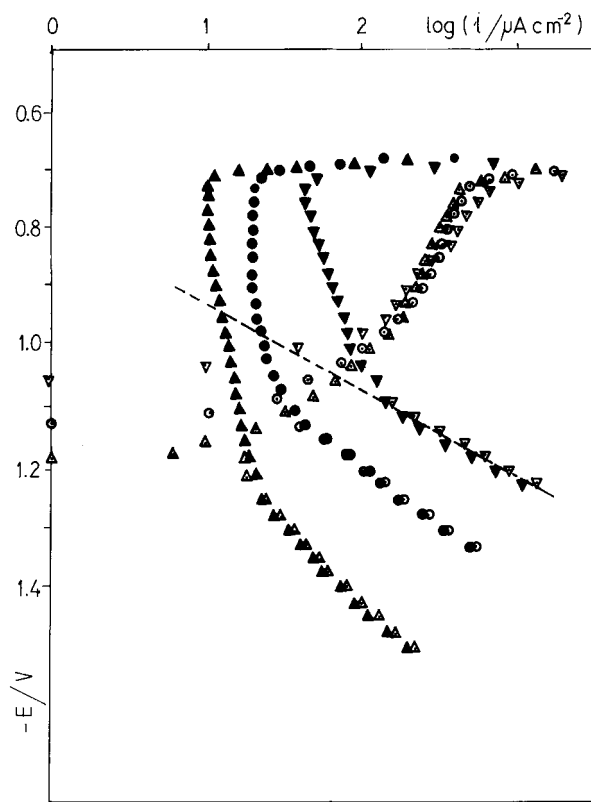


Fig. 5. Cathodic and anodic polarization curves for high purity Al in deaerated NaCl solutions for pH 3, 2 and 1 (▽, ○, △) and simultaneous hydrogen evolution rates detected on the Pt ring (▼, ●, ▲) $v = 10 \text{ mV s}^{-1}$.

rate. The diagram presented in Fig. 4 shows that this is almost correct, that is, changing of the anodic potential from -1.2 to -0.7 V decreases the hydrogen evolution current only by a factor of about 5. As is shown in Fig. 5, a similar situation also exists in more acid solutions, even though the absolute values for the hydrogen evolution currents increase somewhat with decreasing of pH. For example at -0.9 V , a change in pH from 6.5 (cf. Fig. 4) to 1 (Fig. 5) increases i_{H_2} by 70 times, that is, the calculated reaction order with respect to H^+ ions is only $\Delta \log i_{\text{H}_2} / \Delta \text{pH} = (1.9 - 0.45) / (6.5 - 1) \approx 1.45 / 5.5 \approx 0.3$, and so it is not in accord with the expectation for a H^+ discharge process when reaction order one should be obtained. However, if our assumption that this process involving the water dissociation mechanism catalyzed by the adsorption of water molecules within the porous aluminium hydroxide layer is correct, then the observed small increase in the water dissociation rate probably has something to do with the adsorption properties of hydroxide layers formed at different pH values for water molecules. This matter, however, requires additional experimental work for further analysis.

At potentials more positive than E_{pit} , which is approximately the same for all pH values used (-0.75 V), both the Al dissolution and the hydrogen evolution currents suddenly increase. This is related to the range of the pitting Al dissolution mechanism. This change in the Al dissolution mechanism, from

dissolution through the oxide film, in the potential range between E_{cor} and E_{pit} , and by the pitting mechanism for $E > E_{\text{pit}}$ can also be seen in Fig. 6, which shows the time dependence of the anodic Al dissolution currents in neutral solutions for $E = -0.85$ and -0.72 V , in Figs 6(a) and (b), respectively. The steady-state anodic current in Fig. 6(a) indicates dissolution through the oxide film (no pitting), whereas the constant increase of the dissolution current in Fig. 6(b) indicates sporadic formation of pits with a considerable increase of the surface area caused by pitting.

Figures 7(a) and (b) shows the linear i_{H_2} against i_a dependence, for the lower ($i_a < 1 \text{ mA cm}^{-2}$) and higher current density range (up to 50 mA cm^{-2}) as is often observed in the analysis of the negative difference effect [5]. Figure 7(a) shows the negative difference effect in the anodic current density range 0 – 1.2 mA cm^{-2} , in which the corresponding i_{H_2} was experimentally determined by the disc-ring technique, while in Fig. 7(b) the anodic current was expanded to $i_a = 50 \text{ mA cm}^{-2}$, where the i_{H_2} value were obtained from the volumetric measurement of the hydrogen gas evolved during 30 min of anodic polarization in the current density range $i_a = 5$ – 50 mA cm^{-2} . The hydrogen evolution rate, expressed as cathodic current density, was recalculated from the volumetric data by using Faraday law. The use of volumetry at the higher anodic current density was necessary since the ring-disc technique fails to

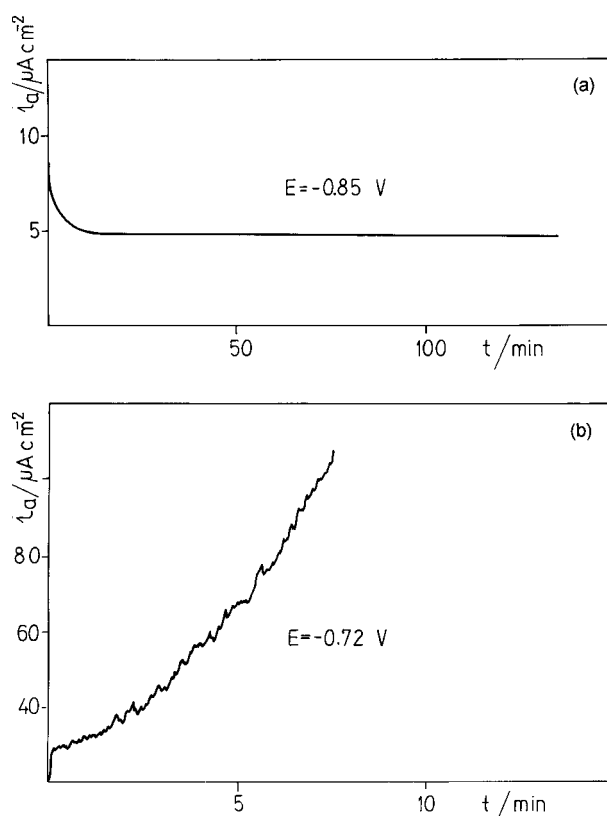


Fig. 6. Anodic current density for high purity Al in NaCl solution as a function of time (a) at $E = -0.85 \text{ V}$ vs SCE (no pitting), (b) -0.72 V vs SCE (with pitting).

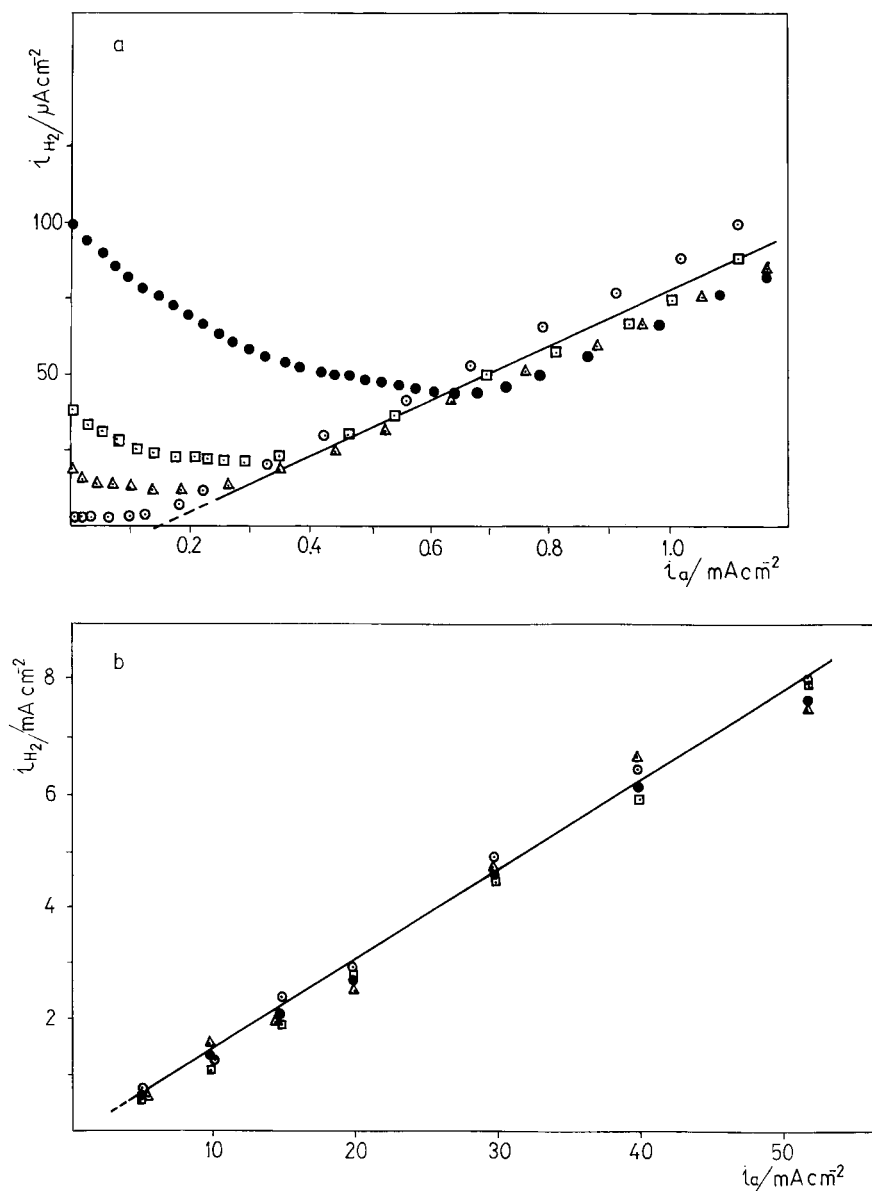


Fig. 7. Simultaneous hydrogen evolution rate (i_{H_2}) as a function of anodic dissolution rate (i_a) (negative difference effect) for high purity Al in NaCl solution of different pH's. (a) Anodic current range 0–1 $mA cm^{-2}$. Data for i_{H_2} obtained by the disc-ring technique. (b) Anodic current range 5–50 $mA cm^{-2}$. Data for i_{H_2} obtained by hydrogen gas volume measurements. pH: (●) 1, (□) 2, (△) 3 and (○) 6.5.

properly collect the hydrogen evolved at the disc when intensive bubbling at the disc occurs (i.e., at about 0.5 $mA cm^{-2}$) of the hydrogen evolution current [6].

It is interesting that all hydrogen evolution currents for anodic current densities larger than that for the pitting potential (which is about -0.75 V), follow the same straight line dependence up to 50 $mA cm^{-2}$. In other words, the negative difference effect, which can be expressed either as $\Delta i_{H_2}/\Delta i_a = 0.11$ or 11% (expressed as the percentage of the overall i_a used to compensate hydrogen evolution, or more simply the decrease of anodic current efficiency), is independent of the solution pH and is related exclusively to the pitting potential range. At potentials more negative than E_{pit} , i_{H_2} decreases in a manner already discussed in connection with the data shown in Figs 3 and 4.

Introduction of small amounts of other components into the Al seems to have two different effects. As shown in Fig. 8 curve 1 (and the corresponding curve 2 for i_{H_2} detected on the Pt ring) for technical grade Al (main impurities Fe, Zn and Cu) is almost the same as for high purity Al on the anodic side, (cf. Fig. 4) including the pitting potential, while a considerable increase in the cathodic hydrogen evolution can be seen. In other words, these impurities catalyse the hydrogen evolution reaction during cathodic polarization but have no effect on the anodic dissolution rate. A small amount of In (0.074%), however, has an effect on both processes, anodic dissolution and cathodic hydrogen evolution, as well as causing a considerable shift of the pitting potential (by about 0.2 V) in the negative direction (see Fig. 8, curve 3, and the corresponding Pt ring detected hydrogen

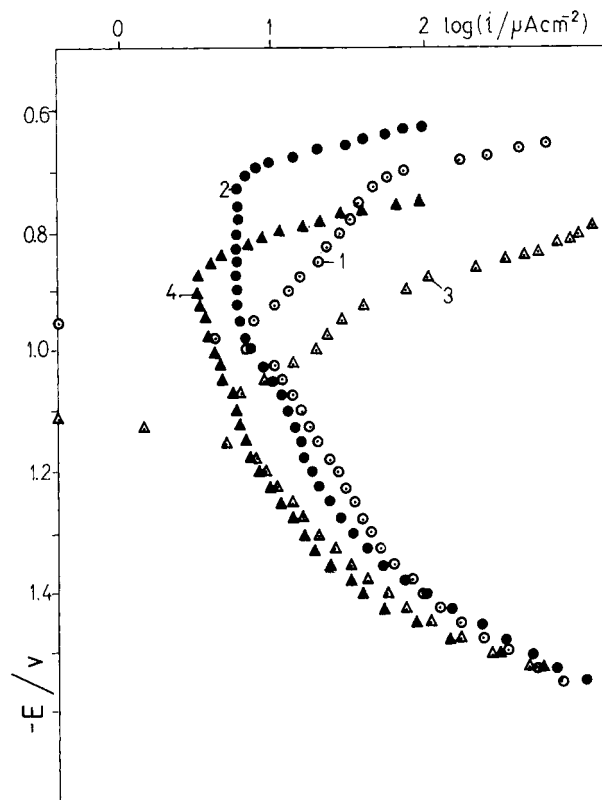


Fig. 8. Cathodic and anodic polarization curves for technical grade Al (AIT) (curve 1) and Al-In alloy (curve 3), and simultaneous hydrogen evolution on AIT (curve 2) and Al-In alloy (curve 4). Key: (○, ●) Al (T); (△, ▲) Al-In.

evolution current, curve 4). Also, the presence of the mentioned impurities has a tendency to decrease the negative difference effect, as shown in Fig. 9 for the three different materials in 0.5 M NaCl solution. The interesting point is that all the mentioned impurities

increase the hydrogen evolution current, but decrease the negative difference effect.

4. Discussion

4.1. Corrosion rate

Previous preliminary results [6] and the more elaborate application of the ring-disc technique for the detection of hydrogen evolved on an Al disc, either during spontaneous corrosion or even during anodic polarization of Al have shown that this technique has successfully opened the possibility of studying corrosion processes with hydrogen evolution at rates between 1 and 500 $\mu\text{A cm}^{-2}$. Bubbles which form on the disc when hydrogen evolves at higher rates escape the Pt ring surface and remain undetected, that is, the collection efficiency of the ring deviates from the theoretically expected value in an unpredictable way.

As shown in Fig. 2, the mean corrosion rate of high purity Al in 0.5 M NaCl (pH ~ 6.5) was about 5 $\mu\text{A cm}^{-2}$. A similar value was obtained by Kunze [12] by the weight loss measurements of 99.99% Al in deaerated 0.5 M NaCl. He also showed that the anodic dissolution rates at potentials in the vicinity of the corrosion potential are about 3.7 $\mu\text{A cm}^{-2}$. Di Bari and Read [13] also obtained a similar dissolution rate in a NaCl solution of pH 4 ($i_a = 10 \mu\text{A cm}^{-2}$).

We hypothesized in earlier papers [1, 3] that at the corrosion potentials in neutral solutions, the hydrogen evolution reaction is neither controlled by H^+ ion discharge (the concentration of H^+ ions at pH 6.5 is too small to sustain a corrosion rate of several $\mu\text{A cm}^{-2}$) nor by direct H_2O discharge, as usually accepted for neutral and alkaline solutions. A practically independent hydrogen evolution process,

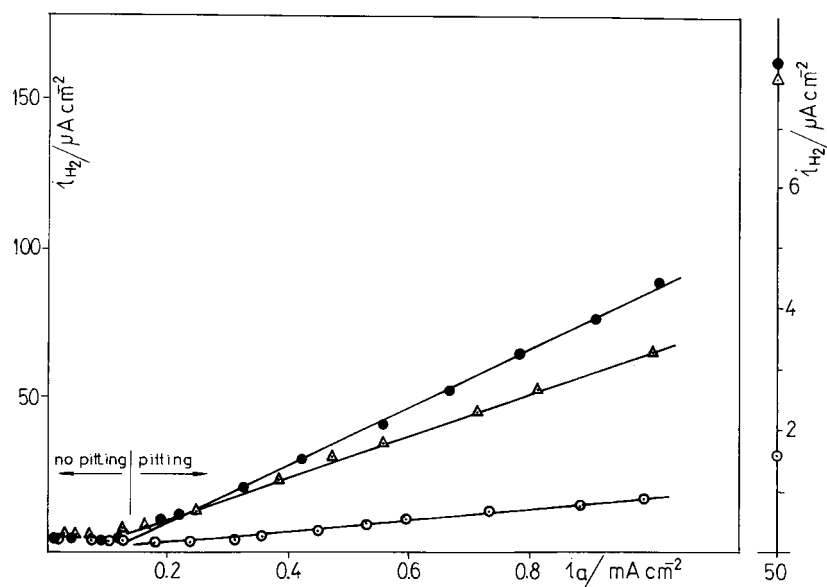
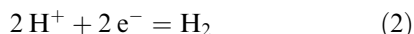
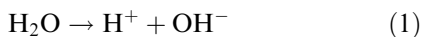


Fig. 9. Negative difference effect for high purity Al, AIT and Al-In alloy in neutral NaCl solutions measured by disc-ring technique. On the right-hand side data for i_{H_2} at 50 mA cm^{-2} obtained by hydrogen gas volume measurements. Key: (●) Al 99.999%; (○) 99.999%–0.074% In; (△) 99.5%.

documented elsewhere [1, 3] and also in Fig. 4, supports the idea that the cathodic process in the potential range $E_{\text{cor}}-E_{\text{pit}}$ proceeds by a water dissociation mechanism



in which the H_2O dissociation rate is rate controlling, while the direct charge transfer process proceeds by one of the known mechanisms (Volmer–Heyrovsky or Volmer–Tafel [11]). Hence, the corrosion rate of Al in neutral solutions is controlled by the H_2O dissociation rate, which is about 10 000 times faster than in the bulk and is probably catalysed by adsorption of H_2O within the pores of the porous part of the aluminium hydroxide layer which is spontaneously formed at the surface. In this context, it should be emphasized that the hydrogen evolution rate in more acid solutions at -0.9 V (Fig. 5) is pH dependent with an apparent reaction order with respect to H^+ ions of about 0.3 which has no rational meaning for any known hydrogen evolution reaction mechanism [11]. One possible explanation for the small increase in the water dissociation rate lay in the fact that the ‘point of zero charge’ for Al oxide is about pH 7, and that in more acidic solutions changes in the electric field in the double layer affect the energy of adsorption of H_2O dipoles and, hence, affect the energy of activation of the dissociation reaction. This is, however, only one rational possibility which needs much more work and a more serious proof.

4.2. Negative difference effect

As pointed out before, the negative difference effect is the phenomenon when the H_2 evolution reaction rate does not decrease with increasing anodic polarization, as expected by the Wagner–Traud mixed potential model (that was named the positive difference effect [2]), but simultaneously increases with the anodic, Al dissolution current density. This increase often appears to be in a linear relation with the anodic current density (i.e., $i_{\text{H}_2} \approx ki_a$), where k depends on the experimental conditions, predominantly on the composition of the dissolving material. Typical values for k are between 0.01 and 0.2 [2]. Aluminium and its alloys are often used in chemical power sources or as sacrificial anodes for corrosion protection [5]. In the relevant literature the same effect is also discussed in terms of the anodic current efficiency being lower than 100% because of the simultaneous hydrogen evolution even at high anodic current densities. Whatever terminology used, the effect is the same and needs clarification.

At this moment, we are not able to make a complete picture of the occurrences related to the negative difference effect. However, our experiments allow some conclusions to be drawn related to it.

First, the results presented in Fig. 6 show that pitting appears only at potentials more positive than

E_{pit} . This is also supported by microscopic observations of the Al surface after anodic polarization in the region $E_{\text{cor}}-E_{\text{pit}}$. Therefore, pitting does not occur during the spontaneous corrosion of pure Al in neutral solution. Simultaneously this means that Al anodically dissolves through the oxide film. The linear Tafel plot with the rather high slope of about $350-400 \text{ mV dec}^{-1}$ is in accordance with the Cabrera and Mott [14] equation for the rate determining ionic transport through an oxide.

Secondly, the appearance of the negative difference effect is obviously related to the pitting dissolution mechanism. This is in accordance with microscopic observations [15] where in an *in situ* experiment, gas bubbles were observed coming out of the pits, with the subsequent analytical proof that the gas in the bubbles was only hydrogen.

Thirdly, Kaesche [16] proposed that the hydrogen evolution from the bottom of the pits is caused by an increased H^+ discharge rate due to the high local anodic current density and to the slow diffusion of Al^{3+} ions out of pit which, on hydrolysis with H_2O , acidifies the solution at the pit bottom. However, the lowest pH which can be achieved by Al^{3+} ion hydrolysis is at maximal expected anodic density in the pit about pH ~ 3 [17]. The fact, shown in Fig. 7, that the negative difference effect does not depend on pH even for pH 1.0, seems to rule out the argument raised by Kaesche.

Fourthly, the impurities in the technical grade Al and the small amount of In accelerate to approximately the same degree the H^+ discharge reaction (Fig. 8) in the cathodic region, but affect quite differently the negative difference effect (Fig. 9), see also [18, 19]. If Kaesche’s model would be operative one should expect higher hydrogen evolution rates, i.e., larger negative difference effects, for both impure materials as compared to the high purity Al. Our experiments show the opposite, a larger negative difference effect is observed for high purity Al.

5. Conclusions

The following can now be stated:

- (i) The rotating Al-disc/Pt-ring technique was shown to be very useful for the determination of corrosion rates and negative difference effect up to $i_{\text{H}_2} \approx 0.5 \text{ mA cm}^{-2}$.
- (ii) Corrosion rates of Al (99.999%), Al (99.5%) and Al–In alloy (0.047%) in deaerated NaCl solutions do not differ very much ($5-10 \mu\text{A cm}^{-2}$).
- (iii) Decrease of the solution pH increases the corrosion rate.
- (iv) Impurities in the electrode material accelerate the cathodic hydrogen evolution.
- (v) There is no pitting between the corrosion and pitting potentials.
- (vi) There is no negative difference effect without the appearance of pits.

- (vii) The negative difference effect does not depend of solution pH between 6.5 and 1.0.
- (viii) Impurities in the Al alloys used only decrease the negative difference effect, in particular In.

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